

EFFECT OF A METAL DEACTIVATOR FUEL ADDITIVE ON FUEL DEPOSITION IN FUEL ATOMIZERS AT HIGH TEMPERATURE

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By

C.A. Moses

Belvoir Fuels and Lubricants Research Facility (SwRF)
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Fuel additives that are metal deactivators have been shown to improve the thermal stability breakpoint temperature of aviation fuels as determined in the Jet Fuel Thermal Oxidation Tester (JFTOT). These additives, therefore, offer the opportunity to upgrade fuels of marginal thermal stability. However, concern has been expressed over whether this upgrade would be realized in actual aircraft hardware. To address this concern, an experimental project has been conducted with fuel atomizers from the T700 engine to determine the effect of the additive DMD-2, a metal deactivator, on high-temperature fuel deposition. The tests were conducted with JP-5 fuel supplied by the Naval Air Warfare Center Aircraft Division, Trenton (NAWCADTRN). For some of the tests, the base fuel was contaminated with copper to a concentration between 400 and 500 ppb. In the uncontaminated fuel, the metal deactivator (MDA) additive was tested at a concentration of 1 ppm; in the contaminated fuel, MDA concentrations of 1 ppm and 5.7 ppm were tested.			
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19. ABSTRACT

With uncontaminated fuel, the results showed that initially the additive significantly reduced the deposition rate, but then, after an induction period, the deposition rate sharply increased. With the copper-contaminated fuel, at 1 ppm, the additive showed a small effect, but did not completely passivate the copper. At 5.7 ppm, there was no significant deposition during the test, indicating the copper was passivated.

It is concluded that the metal deactivators inhibit deposition for a period of time until the surface becomes coated with carbon deposition, and then they no longer serve any function. These results are consistent with some single-tube heat exchanger experiments reported in the literature.

EXECUTIVE SUMMARY

Problems and Objectives: Fuel atomizers are considered the most critical component in an aircraft fuel system since fuel temperatures are the highest and flow dimensions are the smallest. Deposits can affect atomizers by decreasing the flow rate through the atomizer and by causing the flow divider valve, if present, to stick, thus altering the dynamics of throttle response. Deposits can also disrupt the fuel spray and combustion patterns, leading to hot streaks or increased pattern factor, resulting in premature failure of liners, turbine blades, and guide vanes.

Importance of Project: The presence of copper in jet fuel is known to reduce the thermal stability of the fuel because the copper acts as a catalyst, enhancing the oxidation reactions. The objective of this project was to determine the effect of a metal deactivator, MDA, on the hot-fue deposit formation in a gas-turbine fuel atomizer.

Technical Approach: The basic concept of the approach was to compare the flow histories of two atomizer experiments conducted under the same conditions except that neat fuel was flowed through one atomizer while the fuel flowed in the other atomizer contained the additive at the prescribed concentration. The flow histories were determined by recalibrating the atomizers or a flow bench each morning, after they had cooled overnight; the atomizers were then remounted on the test stand and the test resumed. The tests were generally run until the flow rate had deteriorated about 10 percent.

Accomplishments: The major conclusions that can be drawn from this study are: (1) MDA when added to marginal thermal stability fuels will initially inhibit deposition in a fuel injector but after the initial induction period, the deposition rate will proceed at a rate similar to or greater than caused by the fuel without MDA; (2) The improvement in thermal stability caused by the addition of MDA observed in the fuel injector is not as significant as that observed in the JFTOT; and (3) For copper-contaminated fuel, the presence of MDA in sufficient concentration will chelate the copper and inhibit deposition in the fuel injector for a minimum of the 70 hours tested in this study.

Military Impact: The results of this study suggest that under certain circumstances military aircraft can safely operate using a marginal thermal stability fuel that has been treated with MDA. However, due to the potential for extensive fouling that could result in certain cases, unrestricted use of MDA is not advised at this time.

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FOREWORD

This work was conducted at the Belvoir Fuels and Lubricants Research Facility (BFLRF) located at Southwest Research Institute (SwRI), San Antonio, Texas, under DOD Contract Nos. DAAK70-87-C-0043 and DAAK70-92-C-0059. The project was administered by the U.S. Army Belvoir Research, Development and Engineering Center (Belvoir RDE Center), Fort Belvoir, Virginia 22060-5606, with Mr. T.C. Bowen, SATBE-FL, serving as the contracting officer's representative. This program was funded by the Naval Air Warfare Center Aircraft Division, Trenton, NJ, with Mr. R. Kamin, Code PE-33, serving as technical monitor. This report covers the period of performance from November 1990 to August 1992.

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I. INTRODUCTION

The thermal stability of fuel is a measure of the tendency to degrade and form deposits at high-temperature conditions. Fuel atomizers are considered the most critical component in an aircraft fuel system since fuel temperatures are the highest and flow dimensions are the smallest. Deposits can affect atomizers in two ways: (1) by decreasing the flow rate through the atomizer, and (2) by causing the flow divider valve, if present, to stick, thus altering the dynamics of throttle response. Deposits can also disrupt the fuel-spray and combustion patterns, leading to hot streaks or increased pattern factor, resulting in premature failure of liners, turbine blades, and guide vanes.

The thermal stability of the Navy's aviation turbine fuel is controlled by the Jet Fuel Thermal Oxidation Test (JFTOT) according to ASTM Method D 3241 as prescribed by the fuel specification MIL-T-5624. This procedure has been generally effective since few field problems are reported. However, in recent years an increasing number of concerns related to fuel thermal stability have been presented to the Naval Air Warfare Center Aircraft Division, Trenton (NAWCADTRN), which has the responsibility for fuels technology in the Navy. A few of the concerns are the following:

- The use of F-76 in aircraft as an emergency fuel
- The presence of copper in aviation fuel on board ship
- The use of JP-5 that has reduced thermal stability due to shipping or storage.
- The effect of increased heat loads to be placed on the fuel in future aircraft (e.g., AX).

F-76 is a middle distillate or diesel fuel that is normally used for ship propulsion. One of the major concerns over using this category of fuel in aviation systems is that the specification for this fuel has no requirement for thermal stability.^{(1)*} Sometimes the fuel has a thermal stability that meets the JP-5 specification, but more often than not, it will be significantly lower.

* Underscored numbers in parentheses refer to the list of references at the end of this report.

The presence of copper in jet fuel is known to reduce the thermal stability of the fuel because the copper acts as a catalyst, enhancing the oxidation reactions.(2) As little as 50 ppb of copper has been shown to cause a fuel to fail the JFTOT test.(3) As a result, great effort is taken to prevent aircraft turbine fuel from coming in contact with copper during refining, shipping, and storage. On board ship, however, it is common design practice to use copper/nickel alloy in plumbing to avoid corrosion. Organic acids in the fuel cause some copper to dissolve and form soluble organo-metallic compounds such as naphthenates. In a study conducted by the U.S. Army Belvoir Fuels and Lubricants Research Facility for the Naval Air Propulsion Center, fuel samples were collected from aircraft carriers and refueling ships and analyzed for copper, among other things.(3) Many of the carrier samples contained between 300 and 500 ppb of copper, with one sample having over 800 ppb.

Recent studies have shown that a DuPont fuel additive, DMD-2, a metal deactivator (MDA), is not only effective at chelating soluble copper but also in improving the JFTOT breakpoint temperature of uncontaminated fuels by as much as 45° to 50°C.(4,5) Tests with single-tube heat exchangers have also shown that MDA reduces the deposit rates (5,6); however, after an induction period, the deposits form at a higher rate, similar to that observed in the absence of MDA.(6-8) It has been suggested that the MDA is passivating the deposit surface, but that once sufficient fuel lacquer had coated the surface, the passivation ceased to be a factor in retarding deposition.(9)

A number of studies have been conducted, primarily at the Naval Research Laboratory in the U.S. and at the British Petroleum and Shell Thornton Research Centres in the United Kingdom, to determine the mechanisms involved in the action of MDA on thermal stability when copper is not present in the fuel.(4,9,10) Baker, et al. (4) used Laser Ionization Mass Analysis (LIMA) to detect the presence of MDA on the surface of both stainless steel and aluminum JFTOT tubes. Schreifels, et al.(10) showed that MDA inhibited deposition with some fuels, but not with others, suggesting that the effects of MDA are due to interactions in the liquid phase rather than at the surface. They also showed that the MDA on the surface of JFTOT tubes was sparsely distributed, and, in itself, could not have significantly changed the surface. Clark, et al. (9) proposed a two-stage mechanism wherein the MDA first deposits on the surface at available sites

and then subsequently, at elevated temperatures, polymerizes to form an MDA matrix or surface that is less favorable to fuel lacquer formation. The induction period is then explained by the eventual covering of the MDA layer. Baker, et al. (4) also suggested that some decomposition might be going on within the deposit, which could account for the low concentrations of MDA present. For a more complete rendering of the effects of MDA on thermal oxidative stability, the reader is referred to a recent ASTM publication by Hazlett, Chapter IX.(11)

The major concern addressed in this study is if the benefits of MDA on thermal stability that have been demonstrated on the JFTOT and other rigs will be realized in actual fuel atomizers from aircraft engines. This report presents the results from a series of tests to evaluate the effect of MDA on the fouling rate of fuel atomizers from the General Electric T700 engine.

II. OBJECTIVE AND SCOPE

The objective of this project was to determine the effect of the DuPont additive DMD-2, a metal deactivator, on hot-fuel deposit formation in a gas-turbine fuel atomizer. Deposition was determined by repeated calibrations of the test atomizer throughout a test to measure the reduction in flow rate.

Two areas of impact were studied by using both a clean JP-5 fuel and a fuel that was contaminated with copper:

- The effects of MDA on wall passivation were studied by using a clean JP-5.
- The effects of MDA on metal chelation were studied by using a JP-5 contaminated with copper.

III. APPROACH

A. General

The basic concept of the evaluation was to compare the flow histories of two atomizer experiments conducted under the same conditions except that neat fuel was flowed through one atomizer while the fuel flowed in the other atomizer contained the additive at the prescribed concentration. The flow histories were determined by recalibrating the atomizers on a flow bench each morning, after they had cooled overnight; the atomizers were then remounted on the test stand and the test resumed. The tests were generally run until the flow rate had deteriorated about 10 percent.

It was originally planned for the tests to be conducted with the two test atomizers mounted side by side in the same hot-air stream. In previous studies in which only one atomizer was tested at a time, the hot-air stream was provided by a gas-fired burner (e.g., Reference 12). However, in the initial tests in this study, when two atomizers were mounted in the flow, the stem temperatures differed by as much as 50°F. It was first felt that this differing temperature was due to nonuniformities in the airflow from the burner. Inserting a perforated plate upstream of the atomizer mount did not correct the problem.

It was then decided to use a heated sand bath, i.e., a fluidized bed, to create a more uniform temperature environment in which to immerse the two atomizers. This method was successful on the first two sets of tests in which the stem temperatures were within 10°F of each other. It was subsequently determined that the real problem was due to variations in the dimensions of the internal flow passages of the atomizers, leading to variations in heat transfer coefficients. For the evaluations of the copper-contaminated fuel, it was necessary to test the atomizers separately in order to obtain the same stem temperatures on both atomizers.

B. Test Facility

The test facility used was designed and installed at Southwest Research Institute in FY1984 under Department of Defense (DOD) Contract No. DAAK70-82-C-0001. The facility is described in detail in Reference 13 with the exception of one major change. As mentioned previously, the test nozzles are immersed in a heated fluidized sand bath instead of the gas-fired heater for the hot airflow. The facility is shown schematically in Fig. 1.

C. Test Atomizers

The test atomizers were new atomizers supplied by the NAWCADTRN and were production hardware from the General Electric T700 engine. They were manufactured by Parker Hannifin Corporation and identified by FSCM 99207, MFR/PN 4045T30G04. Fig. 2 shows a cutaway drawing of a typical atomizer. This device is a simplex atomizer with an air-blast shroud; there is no flow divider valve to be concerned about in deposition studies. In operation, it acts virtually as a pure air-blast atomizer at idle and in combined mode at high power conditions.

Fig. 3 presents a nominal flow schedule.⁽¹⁴⁾ Also shown are the flow schedules of the specific test atomizers used in this project. As can be seen, there is considerable variation in the actual calibrations; these differences account for the variations in heat transfer discussed earlier.

Before calibrating and testing, the atomizers were flushed with a solvent consisting of toluene, acetone, and methanol to remove any preservatives or oil films that could form deposits independent of the test fuel.

D. Test Fuels

The two base test fuels in which the MDA was evaluated were a JP-5 and a JP-5 contaminated with 300 to 500 ppb of copper. The original plan was that a single JP-5 fuel, supplied by

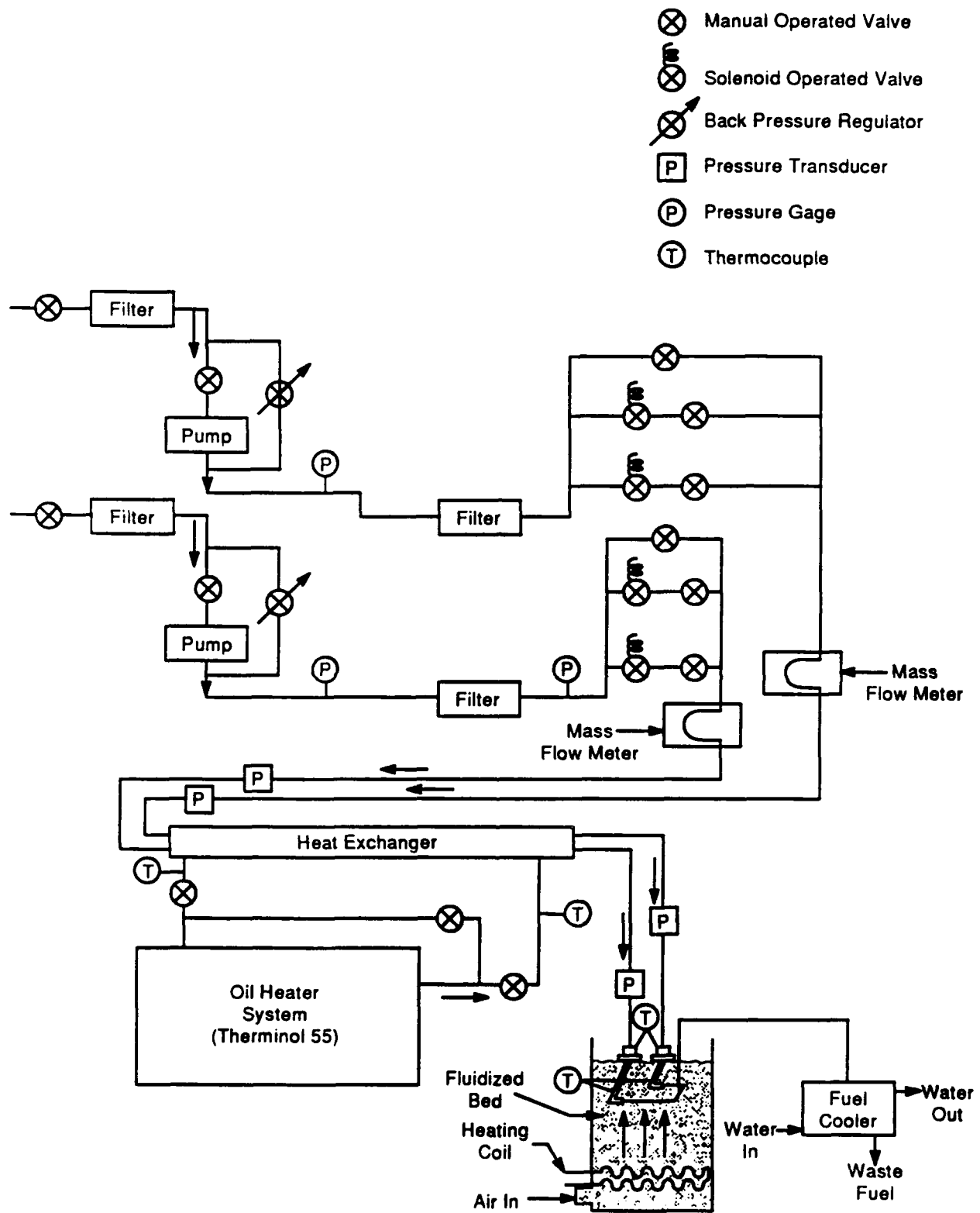


Figure 1. Modified dual hot-fuel nozzle test facility

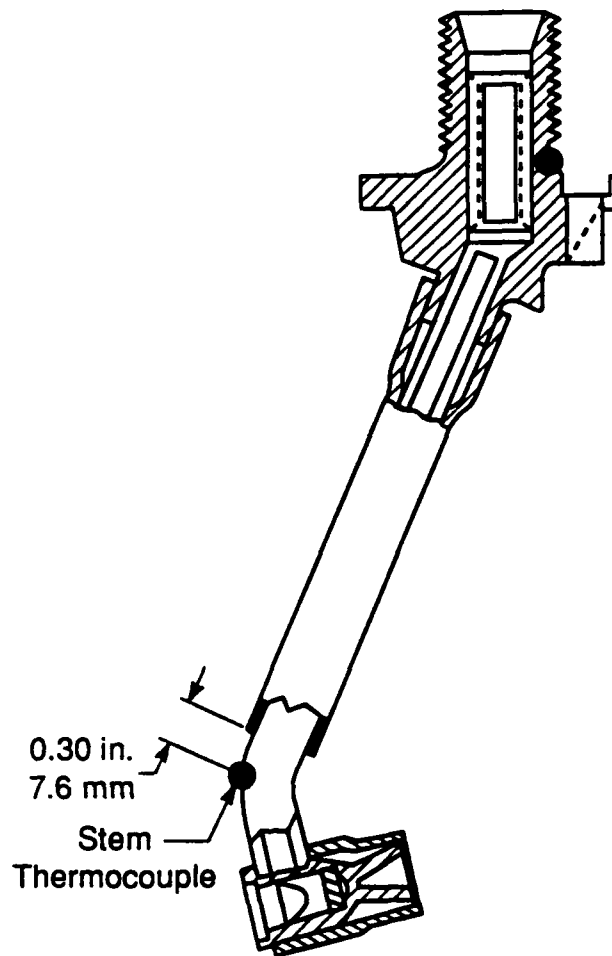


Figure 2. T700 fuel atomizing nozzle

NAWCADTRN, would be used for both the copper-contaminated and uncontaminated tests. This plan, however, did not work due to problems in achieving and maintaining the desired level of copper contamination.

Copper Contamination: The method for contaminating the base fuel with copper followed the procedure used in earlier projects (12) wherein the fuel was exposed to metal turnings (from a lathe) of 90/10 copper-nickel alloy until the copper level in the fuel reached the desired level. The copper-nickel alloy was chosen because the plumbing systems aboard many U.S. Navy ships is fabricated from this alloy according to MIL-C-15726; therefore, the copper would be in the

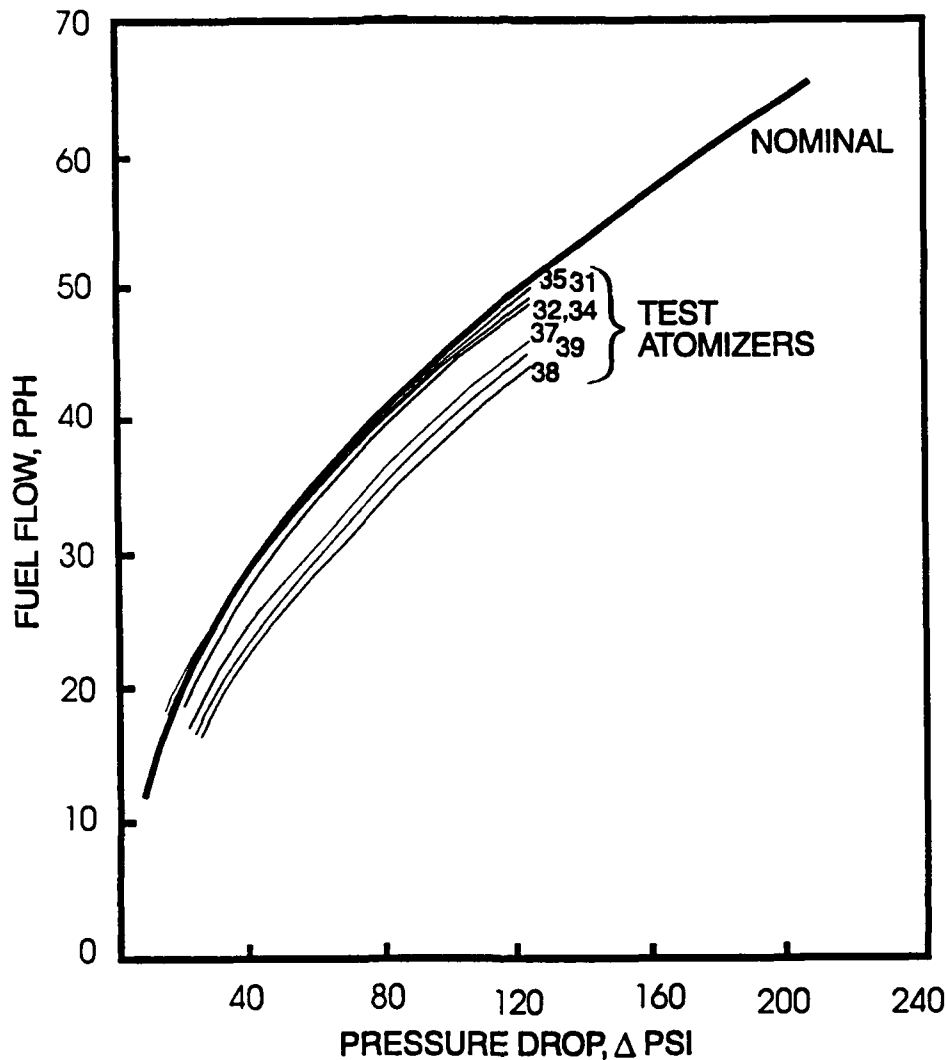


Figure 3. T700 fuel nozzle flow schedules

same form in the test fuel as in real life. The method was to expose the fuel to the copper alloy for a period of time and then circulate the fuel to ensure uniform mixing; then a sample would be removed for analysis and the process repeated until the level of contamination was sufficient. The copper level in the fuel was measured by Induction Coupled Plasma (ICP) spectroscopy. A more detailed description of the procedure for contaminating the JP-5 is provided in the Appendix of this report.

In the initial attempt to contaminate 1,000 gallons of the base fuel, the fuel was exposed to the copper alloy turnings for a total of 346 hours over a period of 4 weeks before obtaining a copper level of 337 ppb. At this time, the pretests were begun to partially foul the test atomizers by

operating on NDF (NATO F-76). Because previous experience with copper-contaminated fuels showed the copper content to sometimes be unstable, the fuel was analyzed to verify the copper content prior to beginning the tests with the copper-contaminated JP-5. The copper level had dropped to 171 ppb. Unfortunately, experience has shown that once a fuel has taken up copper and then began to drop it out, it is very difficult to get it to take up copper again; the organic acids that react with the copper have already been depleted. It was therefore decided that NAWCADTRN would provide another 2,000 gallons of the test fuel.

When the new shipment arrived, 385 gallons were placed in drums and set aside for blending purposes in case the copper level got too high. The basket of copper alloy turnings were placed in the remaining 1,615 gallons of fuel overnight for 16 hours before a sample was taken for analysis. In this short time, the copper content had shot up to 1,247 ppb, and had further increased to 1,412 ppb before the first analysis was received. The 385 gallons of JP-5 set aside was insufficient to blend the fuel back to the desired range of 300 to 500 ppb. The decision was made by the technical monitor at NAWCADTRN not to ship additional fuel but to use JP-5 that was on hand at SwRI as additional blending stock. This decision was made because an earlier 2,000-gallon shipment of fuel was found to contain 138-ppb copper as delivered; it was felt that too much time would be required to sort out that problem and then to ship new fuel. The final blend contained 462-ppb copper. The copper concentration was repeatedly monitored throughout the tests with copper-contaminated fuel; it fluctuated between 414 and 523 ppb. The analysis prior to the last test was 460 ppb.

MDA Addition: For all but the last test, MDA was evaluated at a concentration of 1 ppm; in the last test, it was evaluated at the maximum allowable concentration of 5.7 ppm. To blend the fuel, a measured amount of fuel was placed in a 500-gallon tank and the fuel was pumped around to establish circulation in the tank. Then, the measured amount of MDA was added, and the fuel was circulated for at least 16 hours (overnight). For 378.5 liters (100 gallons) of fuel, 0.31 cm³ was added to achieve a concentration of 1 ppm.

E. Test Procedure

In the initial tests, two atomizers were mounted side-by-side on the holder that supported them in the sand bath. One atomizer was tested on neat fuel, while the other atomizer used the fuel with the additive in the appropriate concentration. Heaters were used on the fuel lines to match the inlet fuel temperatures for the two atomizers. In the later tests, atomizers could not be matched closely enough for stem temperature and they had to be tested separately as discussed earlier.

The test procedure was to first establish the fuel and sand-bath temperatures and then immerse the test atomizer in the sand bath up to the mounting flange. At the end of each day's testing, the heaters were shut off and the atomizers were cooled to ambient temperature while fuel still flowed through them; the atomizers were then removed from the test stand and placed on a calibration stand to determine deterioration in flow performance.

F. Test Conditions

For all the tests, the fuel flow rate was 45 lb/hr and the stem temperature of the atomizer was 700°F (371°C). Every 30 minutes, the flow rate was cycled up and down 10 percent to simulate throttle maneuvers. The fuel temperatures were selected from past experience, based on the JFTOT breakpoint temperature, so the test time would be on the order of 50 to 75 hours. For the uncontaminated fuels, the fuel inlet temperature was 395°F (202°C); for the copper-contaminated fuels, the fuel inlet temperature was 350°F (177°C); the lower temperature is due to the lower JFTOT breakpoint temperature of the copper-contaminated fuel.

The air temperature was determined by controlling the temperature on the upstream side of the atomizer stem to 700°F (471°C); typical bath temperature was 975°F (524°C). The location of the control thermocouple is shown in Fig. 2. The airflow rate through the sand bath was monitored and maintained at a constant rate among the tests to keep the external heat-transfer coefficient as constant as possible throughout the tests.

G. Calibration Tests

Each test atomizer was calibrated for flow rate versus pressure after the thermocouples were attached. Prior to the calibration, the atomizer was flushed with a solvent consisting of toluene, acetone, and methanol. Using a calibration fluid conforming to MIL-C-7024C, Type 2, the atomizers were calibrated at pressures of 25, 50, 75, 100, and 125 psid in both ascending and descending directions; these data generally agreed to within 0.3 percent. The flow rate at 100 psid was used as the base against which reductions in flow rate were determined.

At the beginning of each test day, the test atomizer, which had cooled overnight, was removed from the test stand for calibration. This procedure resulted in test intervals of approximately 8 hours. As in the original calibration, the flow rates were measured at pressure intervals of 25 psi up to 125 psid in both ascending and descending directions.

H. Test Matrix

The overall test matrix is summarized in TABLE 1, which shows the fuel, additive concentration, presence of copper, and nominal test temperatures.

TABLE 1. Summary of Test Conditions

Test No.	Fuel	JFTOT Breakpoint, °F (°C)	MDA, ppm	Cu, ppb	Fuel Temperature, °F (°C)	Stem Temperature, °F (°C)
1	JP-5	475 (246)	--	--	395 (202)	700 (371)
2	JP-5 + MDA	570 (299)	1.0	--	395 (202)	700 (371)
3	JP-5	475 (246)	--	--	395 (202)	700 (371)
4	JP-5 + MDA	570 (299)	1.0	--	395 (202)	700 (371)
5	JP-5 + MDA	570 (299)	1.0	--	395 (202)	700 (371)
6	JP-5 + MDA	570 (299)	1.0	--	395 (202)	700 (371)
7	JP-5 + MDA	570 (299)	1.0	--	395 (202)	700 (371)
8	JP-5/Cu	*	--	460	350 (177)	700 (371)
9	JP-5/Cu + MDA	*	1.0	460	350 (177)	700 (371)
10	JP-5/Cu + MDA	*	5.7	460	350 (177)	700 (371)

* Not determined due to rapid filter plugging.

The purpose of Tests 1 through 4 was to determine the effect of 1 ppm of MDA on deposition/fouling rates of the T700 atomizers, while the purpose of Test 5 was to determine the long-term effects of MDA on deposition. This test was a simple extension of Test 4. The purpose of Tests 6 and 7 was to determine the effect of flowing JP-5 containing MDA through an atomizer that was already partially fouled; for this purpose, the atomizer from Tests 1 and 3 were used. The purpose of Tests 8, 9, and 10 was to determine the effect of MDA on the fouling rates of copper-contaminated fuel. Test 8 established the baseline with no MDA present, while Tests 9 and 10 evaluated the effect of 1- and 5.8-ppm MDA, respectively.

IV. RESULTS

All the results are presented in terms of the percent of flow reduction (at 100 psid) as a function of test time. Note: An increase in flow reduction corresponds to an increase in deposit.

A. JP-5 Plus MDA

Fig. 4 presents the results of Tests 1 and 2 to determine the relative effect of 1 ppm of MDA on deposition. The results of Test 1 show a greater flow reduction than Test 2, indicating a higher rate of deposition. The stem temperature of the atomizer in Test 1 was typically about 70°F higher than that of Test 2, so the tests were repeated to verify that the results were due to the presence of the MDA and not the variation in temperature.

In conducting verification tests, Tests 3 and 4, the atomizers were first checked for relative stem temperature using JP-7 as a test fuel. There was a difference of about 20°F in operating temperature, so the atomizer with the higher temperature was assigned to the flow with MDA, i.e., Test 4. The results of Tests 3 and 4 are presented in Fig. 5. The overall effect was the same despite the temperature reversal. Thus, it is safe to say that the presence of the MDA reduced the deposition rate over the testing period of 67 hours.

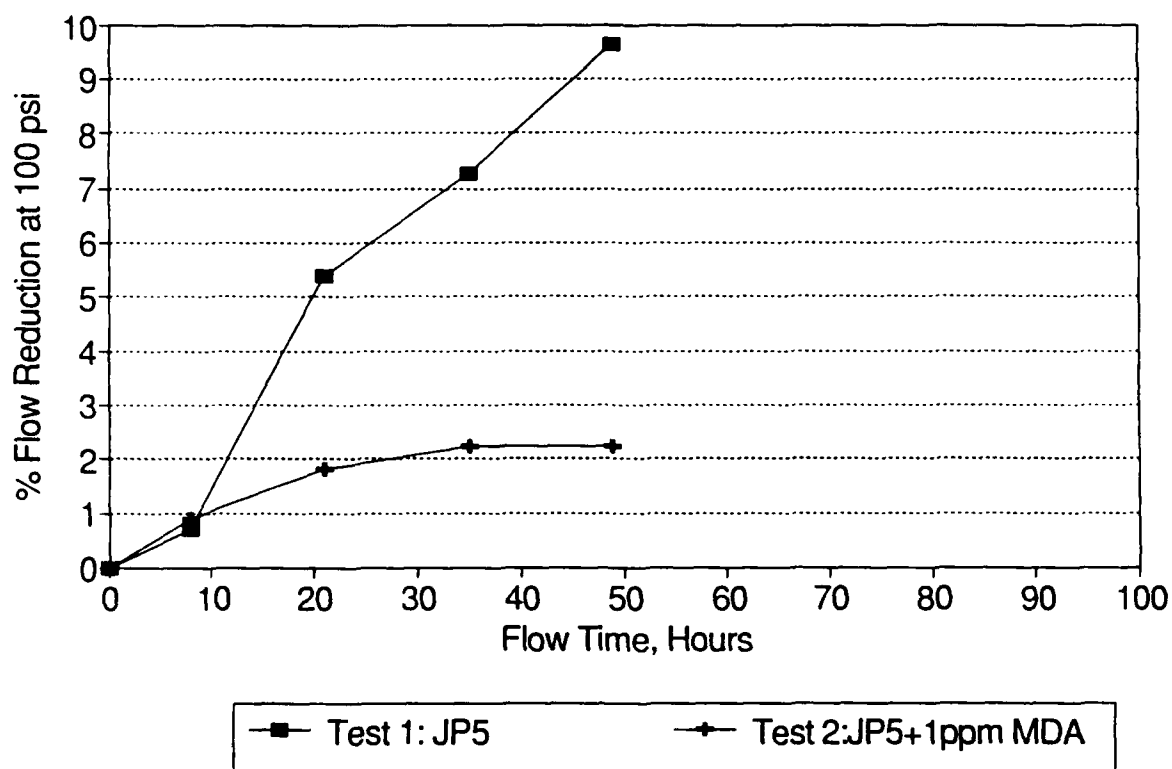


Figure 4. Effect of MDA on deposition

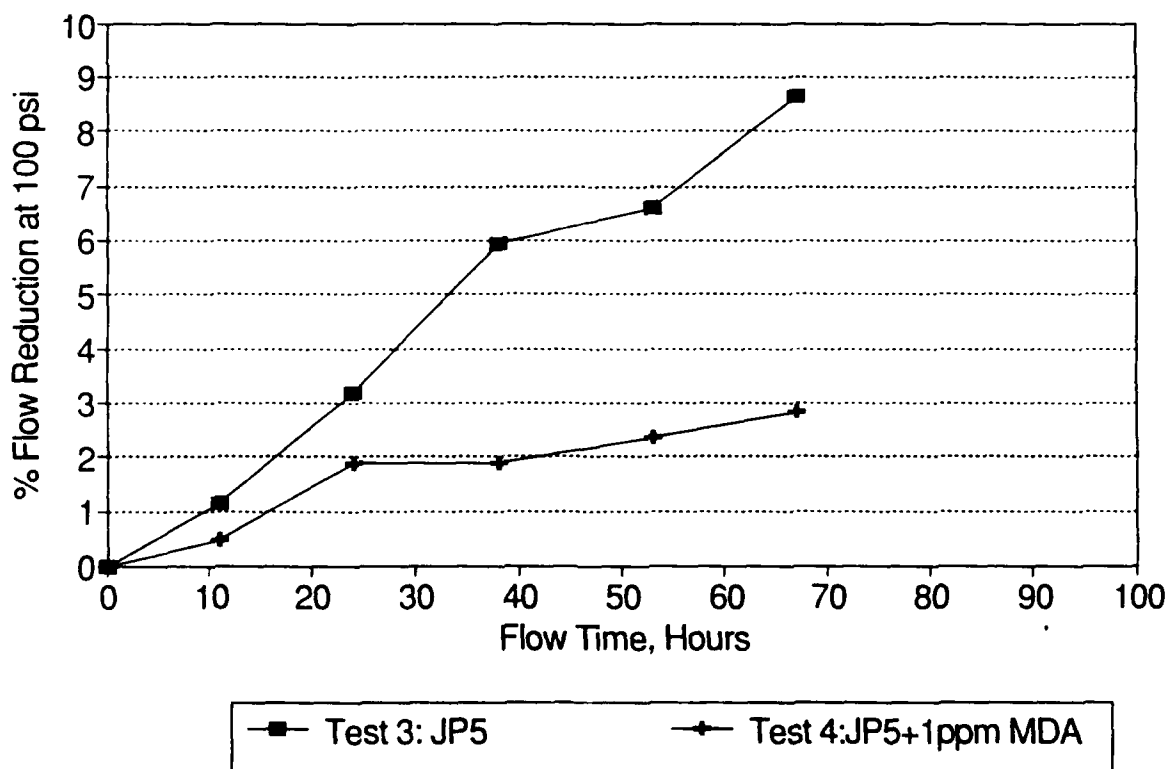


Figure 5. Effect of MDA on deposition

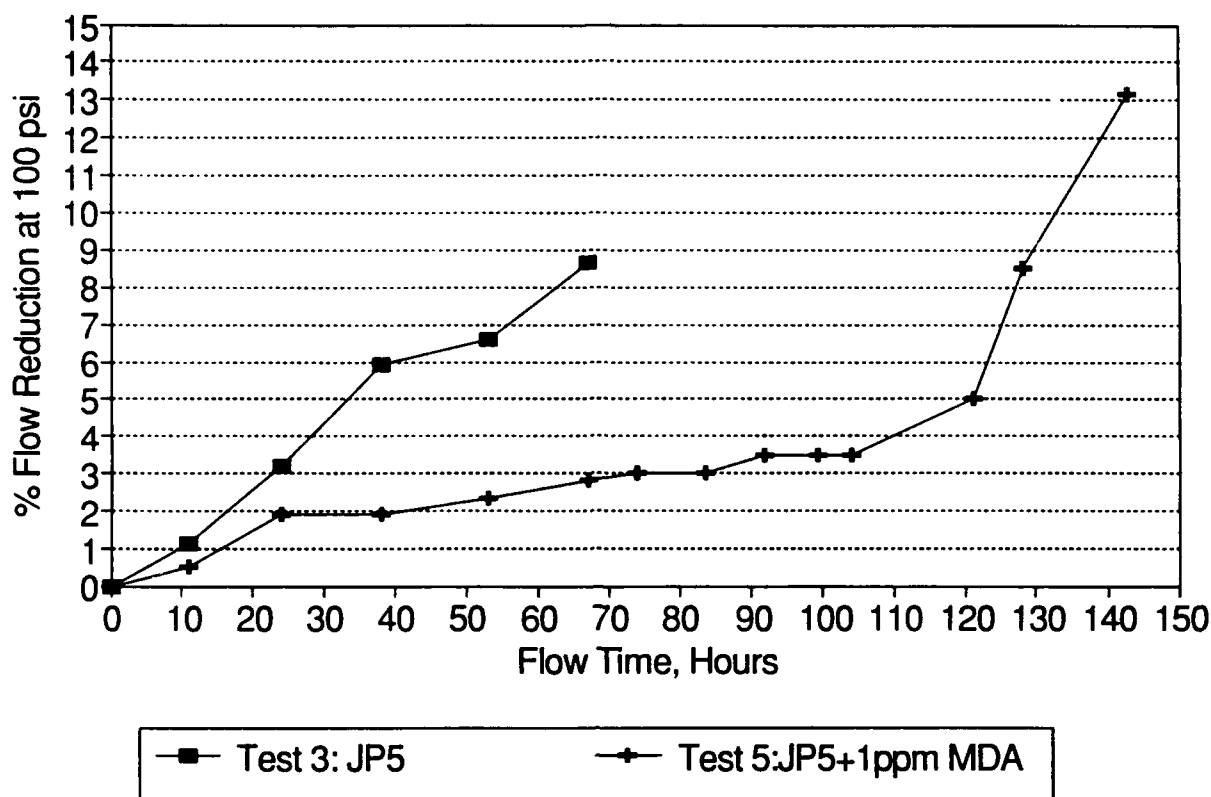


Figure 6. Long-term effect of 1-ppm MDA on deposition

The purpose of Test 5 was to evaluate the longer term effects of MDA on deposition. Fig. 6 presents the results of Test 5, which was simply an extension of Test 4. The results show a continued slow rate of deposition for the first 105 hours. After this time, the rate of deposition rapidly accelerated to a rate three times as high as that of neat JP-5 in Test 3.

Two tests were conducted to determine the effect of using MDA in a used atomizer, i.e., one that was already partially fouled. The atomizers from Tests 1 and 3 were used for this evaluation. The results are shown in Figs. 7 and 8 for Tests 6 and 7, respectively. In Test 6, the flow rate leveled off as soon as the JP-5 plus MDA was introduced, and remained unchanged for about 35 hours before starting to slowly decrease. The test was stopped before a trend could be firmly established. In Test 7, the flow rate began to increase almost immediately after the MDA was introduced; in Fig. 7 this increase is shown as a decrease in the flow rate reduction during the period from 68 to 100 hours. After about 100 hours, the flow rate began to decrease at about the same rate as JP-5 plus MDA additive as in Tests 2 and 4 (see Figs. 4 and 5).

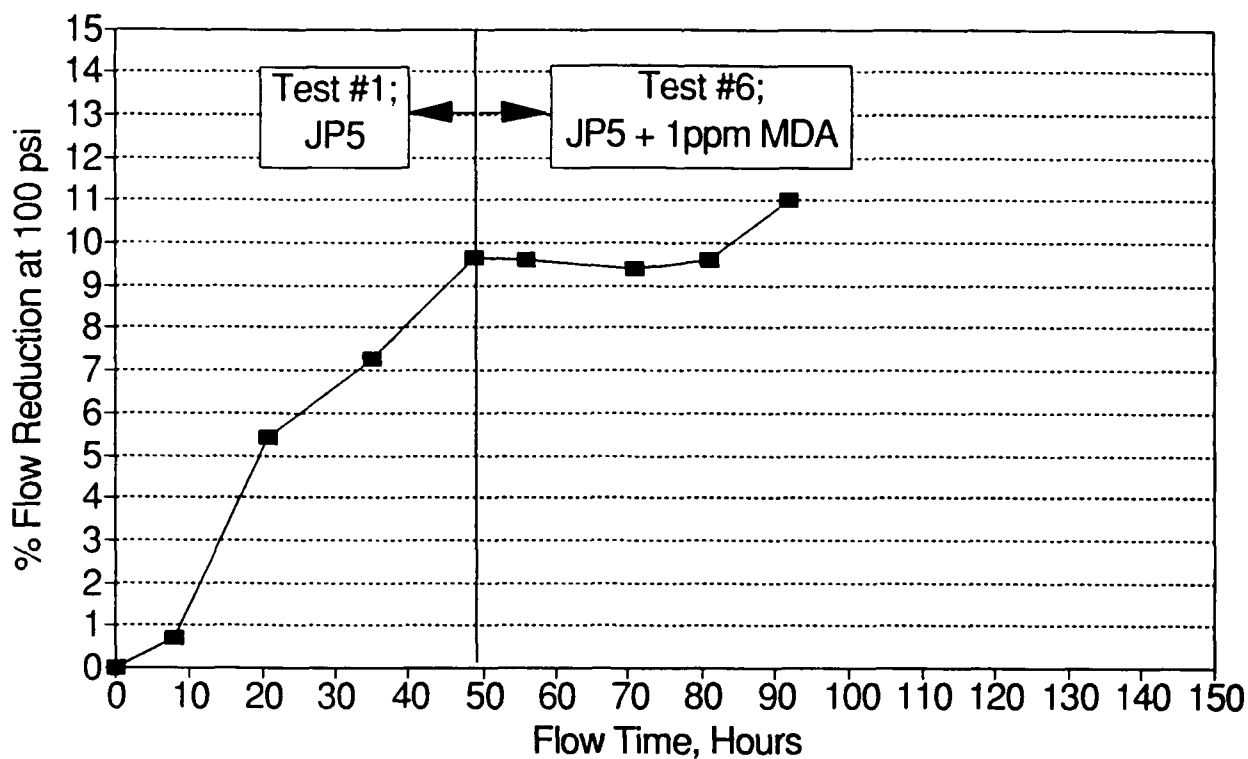


Figure 7. Effect of MDA on deposition in a used nozzle

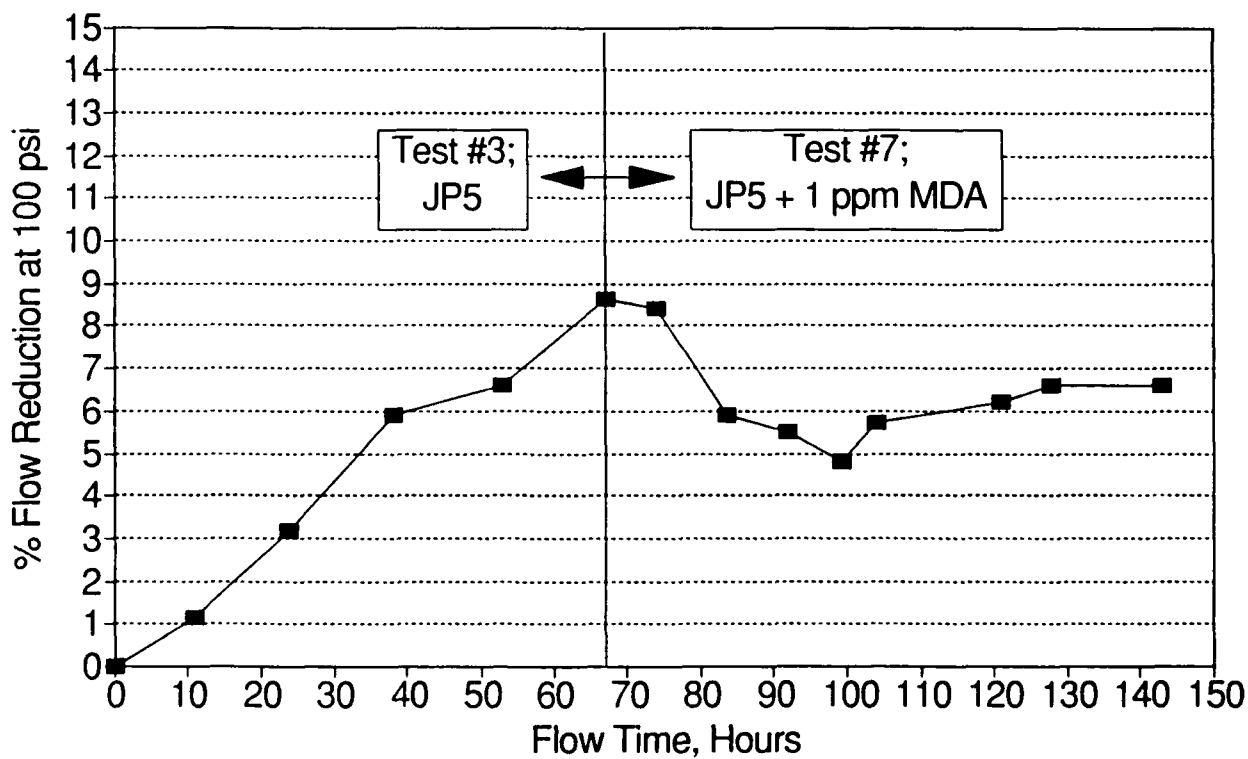


Figure 8. Effect of MDA on deposition in a used nozzle

B. Copper-Contaminated JP-5 Plus MDA

In the tests to determine the effect of MDA on copper-contaminated fuel, the test atomizers were first operated with NDF (F-76) to establish a preliminary deposit such as would be found in a used atomizer in the field; flow reductions due to the prefouling were between 4 and 6 percent. The percent reduction in flow in the following discussion is based on the flow rate at the introduction of the copper-contaminated test fuel, not the flow rate of the new atomizer.

Fig. 9 illustrates the effect of MDA on copper-contaminated fuel by comparing the results of Tests 8, 9, and 10 at three different concentrations of MDA: 0.0, 1.0, and 5.8 ppm. With no MDA, the atomizer immediately began to foul at a relatively high rate, more than five times faster than in Tests 1 or 3, even though the inlet fuel temperature was 50°F lower for the copper-contaminated fuel. The addition of 1 ppm of MDA significantly reduced the deposition rate as shown in the middle graph of Fig. 9, but did not completely passivate the copper. The addition of 5.8-ppm MDA was sufficient to passivate the copper and even improve the flow somewhat in a manner similar to Tests 6 and 7.

V. DISCUSSION

The results of Tests 1 through 4 agree with the results of Clark (5) and Clark, et al. (7) from heated-tube rig data that the presence of MDA in the fuel significantly reduces deposition for fuel with low concentrations of copper but does not prevent deposition; after an initial induction period in which deposition may occur at a relatively low rate, deposition can take place at a significant rate. In Test 5, after a period of about 110 hours, deposition with the fuel containing 1-ppm MDA occurred at three times the rate of the JP-5! Fig. 10 reproduces Fig. 6 except that the fouling rates have been extrapolated in time using least squares fits to the data. This extrapolation suggests that, after 165 hours, the fuel with 1-ppm MDA would actually have created more deposit than the same fuel without MDA!

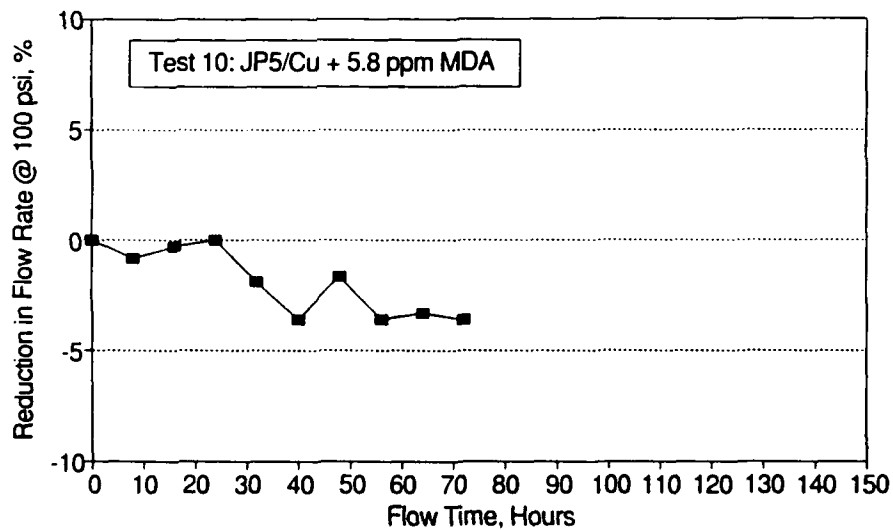
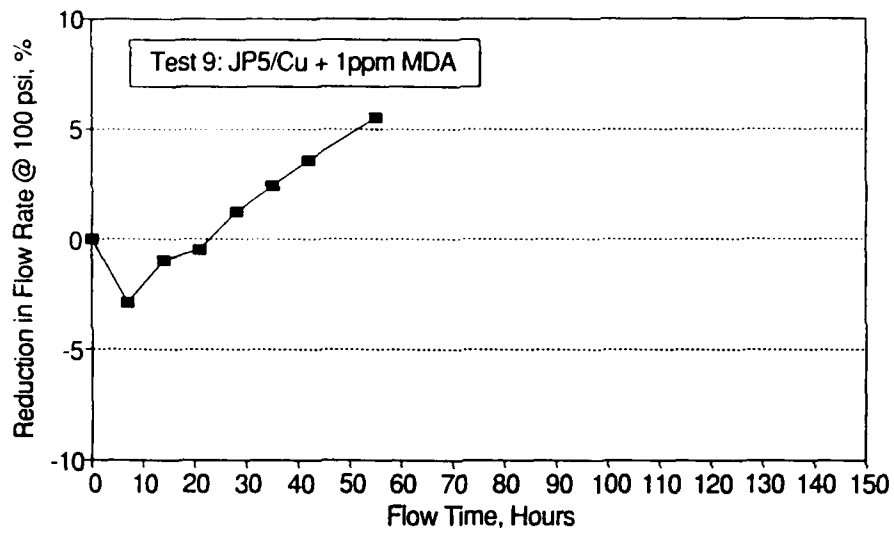
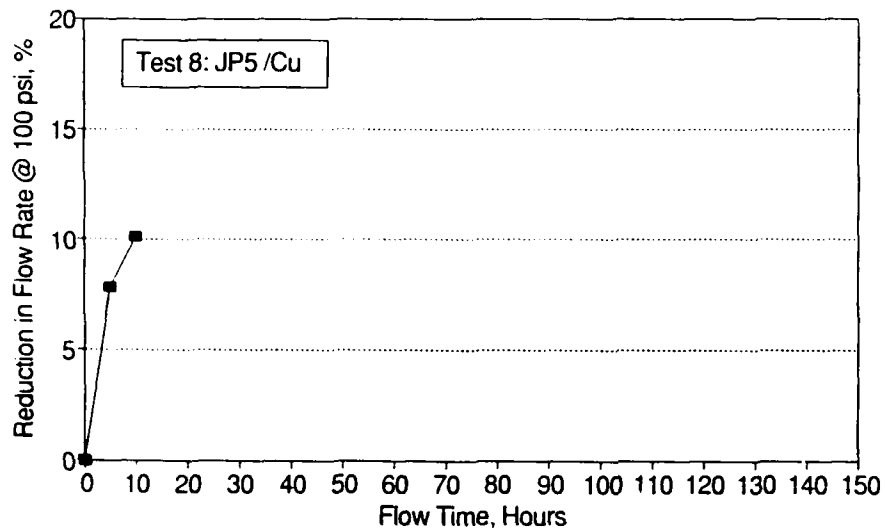


Figure 9. Effect of MDA on deposition with copper-contaminated fuel

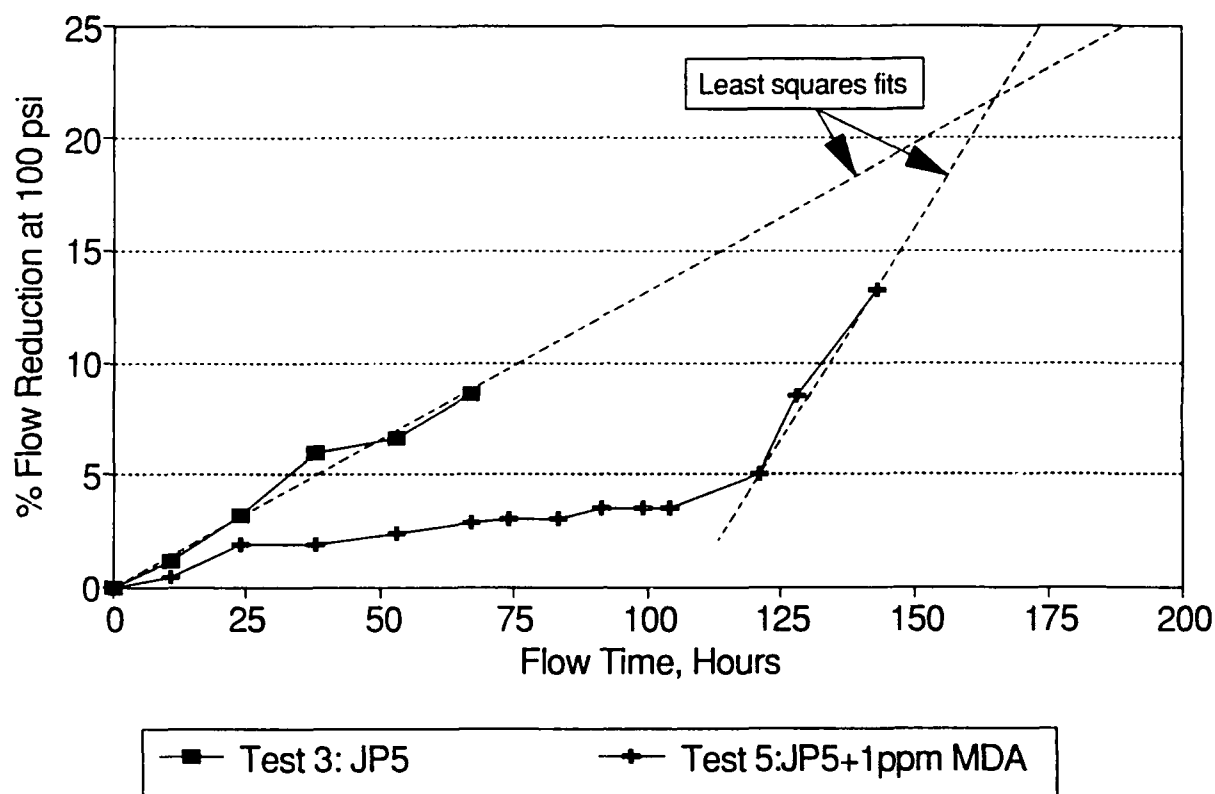


Figure 10. Long-term effect of 1-ppm MDA on deposition

Since these tests were conducted at increased fuel temperatures to accelerate the deposition, the results of Test 5 should be conservative in terms of the induction period and fouling rate. This fact would suggest that aircraft should be able to use marginal fuel that has been upgraded with MDA for many hours without deposition problems, but, at some point in time, the situation may get worse. It is not possible to predict the period of induction from the data reported here because the induction period may depend on the chemistry of the fuel, the temperatures of the fuel and surface, and the metallurgy of the surface. More importantly, nothing is known about the factors affecting the rate of the delayed deposition. Further research is necessary to shed light on the significance of these parameters. Also, long-term effects on filters were not addressed.

The apparent effects of MDA on the flow rate in a used atomizer, or other piece of test equipment, has not been previously reported. Based on the theory that the MDA is passivating the metal surface, it would be expected that MDA would have little effect on a used surface, i.e., one with some deposit on it. However, in the four tests in which "JP-5 plus MDA" were tested in a partially fouled atomizer, a definite effect was noted. To review the immediate effect when

MDA was introduced: In Test 6, there was an initial period of about 30 hours when deposition stopped, i.e., flow rate remained constant, before the flow rate again began to decrease. In Test 7, the flow rate actually increased a few percent before leveling off. In Test 9, with the copper-contaminated fuel, there was a temporary increase in flow rate of a few percent followed by the expected decrease in flow rate. In Test 10, there was an initial period when the flow rate suddenly remained constant for about 20 hours, followed by an increase in flow rate of a few percent, followed by a period of fairly constant flow rate.

The observed increases in flow rate were completely unexpected. It should be noted that in earlier deposition testing at SwRI with T700 atomizers, occasionally an unexplained increase in flow rate would be seen during a test; it was assumed that a piece of deposit had come off or possibly some foreign object left from machining/fabrication had dislodged.⁽¹²⁾ Thus, the observed phenomenon could be hardware related rather than an MDA effect. The fact that something happened immediately after introducing the MDA still leaves the possibility of an MDA effect even though it is unexplained at this time.

The observed leveling of flow rate in Tests 6, 7, and 10 suggests that the effect of MDA is not solely one of surface passivation. This is understandable in Test 10 with the copper-contaminated fuel, where the MDA would be expected to chelate the copper in the bulk. However, the results of Tests 6 and 7 indicate that MDA has an effect even in a system in which the critical surfaces, i.e., where pressure drop is significant, are covered with a deposit. This observation is in disagreement with the conclusions of Clark and coworkers.^(5,6)

Unpublished results from experiments performed by the author with a single-tube heat exchanger suggest that in the thermal oxidation regime, surface reactions are relatively unimportant in deposit formation. If this is true, surface passivation itself by MDA would have little effect on deposition. All of this suggests that MDA may enter into the mechanisms of deposit formation by different means depending on the fuel, the presence of copper contaminants, and the chemical nature of the surface, i.e., bare metal or carbonaceous.

Pursuing an explanation for these results was beyond the scope of this program. However, it is felt that such an explanation is important before claiming benefits of using MDA. Longer term testing may have resulted in accelerated deposition as was found in Test 5.

The results of the tests with the copper-contaminated fuels were in agreement with the literature and showed that MDA in sufficient concentration will chelate the copper and inhibit deposition. Concentration effects were not addressed here but have been shown to be effective at a ratio of 5:1 MDA/Cu by weight or 1.1:1 mole ratio, which agrees with the 1.2:1 ratio claimed by DuPont.⁽⁶⁾ Long-term effects were not investigated, but are warranted in view of the results of Test 5.

As a further note, the atomizers tested in this study have been delivered to the Naval Research Laboratory to be cut open for analysis of the deposits. These results will be reported elsewhere.

VI. CONCLUSIONS

The following conclusions are drawn from this study concerning the effect of MDA on fuel thermal stability and, in particular, the deposition in atomizers:

- For fuels uncontaminated with copper, experiments with single-tube rigs accurately predict the results found in atomizers in that MDA initially inhibits deposition but, after a period of induction, deposition does occur.
- However, based on the results of one long-term test, following the induction period mentioned above, the presence of MDA in a fuel may result in higher deposition rates, eventually leading to a greater reduction in flow rate than if the additive were not used.
- The presence of MDA in the fuel appears to retard deposition even on surfaces that have been partially fouled, i.e., already coated with a hot-fuel deposit. This

observation is not explainable in terms of the current concept of how MDA enters into the deposition mechanism, i.e., by passivating the active sites on the bare metal.

- For fuels contaminated with copper, the presence of MDA in sufficient concentration will chelate the copper and inhibit deposition.

With regard to the last two conclusions, long-term effects such as addressed in the second conclusion were not investigated.

VII. RECOMMENDATIONS

Two questions were identified in this study that, if answered, would aid in the decisions of whether to use MDA to upgrade fuels of marginal thermal stability.

- What parameters affect the induction period and the subsequent high deposition rate? Answering this question is necessary to provide guidance on whether MDA can be safely used to "upgrade" fuel for use in certain aircraft and some limits on the period of use, i.e., engine time.
- Is the apparent initial cleansing effect of MDA on partially fouled atomizers real and what is the mechanism? Answering this question would also affect the decisions on how MDA should be used, and could, if real, lead to some new methods for cleaning atomizers both at squadron level and depot level.

Another question not addressed in this study is the effect of chelated copper on filters; some studies have seen particulates and/or gelled masses on filters; although they did not affect these experiments, the long-term effects apparently have not been investigated.

An experimental program using small heated tubes is recommended for addressing the questions posed above. These tubes would allow control over the test variables and provide surfaces that

can easily be analyzed for deposit mass and chemistry than atomizer tests such as conducted in this study. A filtration experiment should be added to address the other problem.

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APPENDIX

Procedure for Producing Copper-Contaminated JP-5

(Reproduced From Reference 12)

1. Purchase appropriate amount of MIL-C-15726, 90/10 copper-nickel alloy bar stock. Approximately one pound of alloy is needed per twenty gallons of JP-5 to be contaminated.
2. Machine alloy into "cuttings" using a lathe or similar machining technique to produce large amount of alloy surface area for exposure to circulating JP-5. These "cuttings," when collected, will have an appearance, except for color, similar to very coarse steel wool.
3. Place alloy "cuttings" in a container fabricated from expanded metal or screen. This container should have numerous small openings to permit the JP-5 to freely pass over the "cuttings."
4. Place the basket of "cuttings" in the container (tank) containing the measured amount of JP-5. For copper contaminating a small amount of fuel (50 gallons or less), an air-powered stirrer can be employed to mix the fuel, thus causing adequate exposure to the "cuttings" surfaces. For large amounts of fuel, it is recommended that a large tank with pump and plumbing be employed for circulating the fuel. It is preferable to pull from one end of the tank and pump back into the opposite end with the "cuttings" placed in between. Simple ingenuity should be employed for this operation.
5. Leave the alloy in the fuel the appropriate amount of time to obtain the desired amount of copper in the fuel in parts per billion (ppb). This copper content was determined by using a Perkin-Elmer ICP/6000 spectrometer at SwRI, which has a minimum detection level of 2 ppb for copper.
6. Generally speaking, the copper "leaches" into the JP-5 fairly rapidly at first, with a decreasing rate after an initial time interval. Addition of new unused alloy "cuttings" in the fuel accelerates the rate of adding copper to the fuel, at least up to 300 to 400 ppb copper concentration.
7. A graph showing actual and estimated results obtained at SwRI for copper concentration in JP-5 is presented as Fig. A-1. This graph can be employed as a guideline only for copper contaminating JP-5 using the MIL-C-15726, 90/10 copper-nickel alloy described above.

(Added Notes for This Report)

8. It has been seen that, after a period of time, the activity of the "cuttings" is reduced, probably due to corrosion on the surface. The surface can be reactivated by dipping the "cuttings" in a 4-percent solution of hydrochloric acid for about 45 minutes, followed by a 10-percent caustic solution (Noah) to neutralize the acid. Then rinse in water; the "cuttings" should then be placed in an oven to dry before putting them in the fuel.
9. The rate of uptake of copper into the fuel differs widely from fuel to fuel. After a time the copper may come out of solution, but the concentrations are too small to determine exactly where it goes. Also, once the copper concentration falls, it is very difficult to get any more copper into the fuel. Apparently, all the active hydrocarbons have been used up.

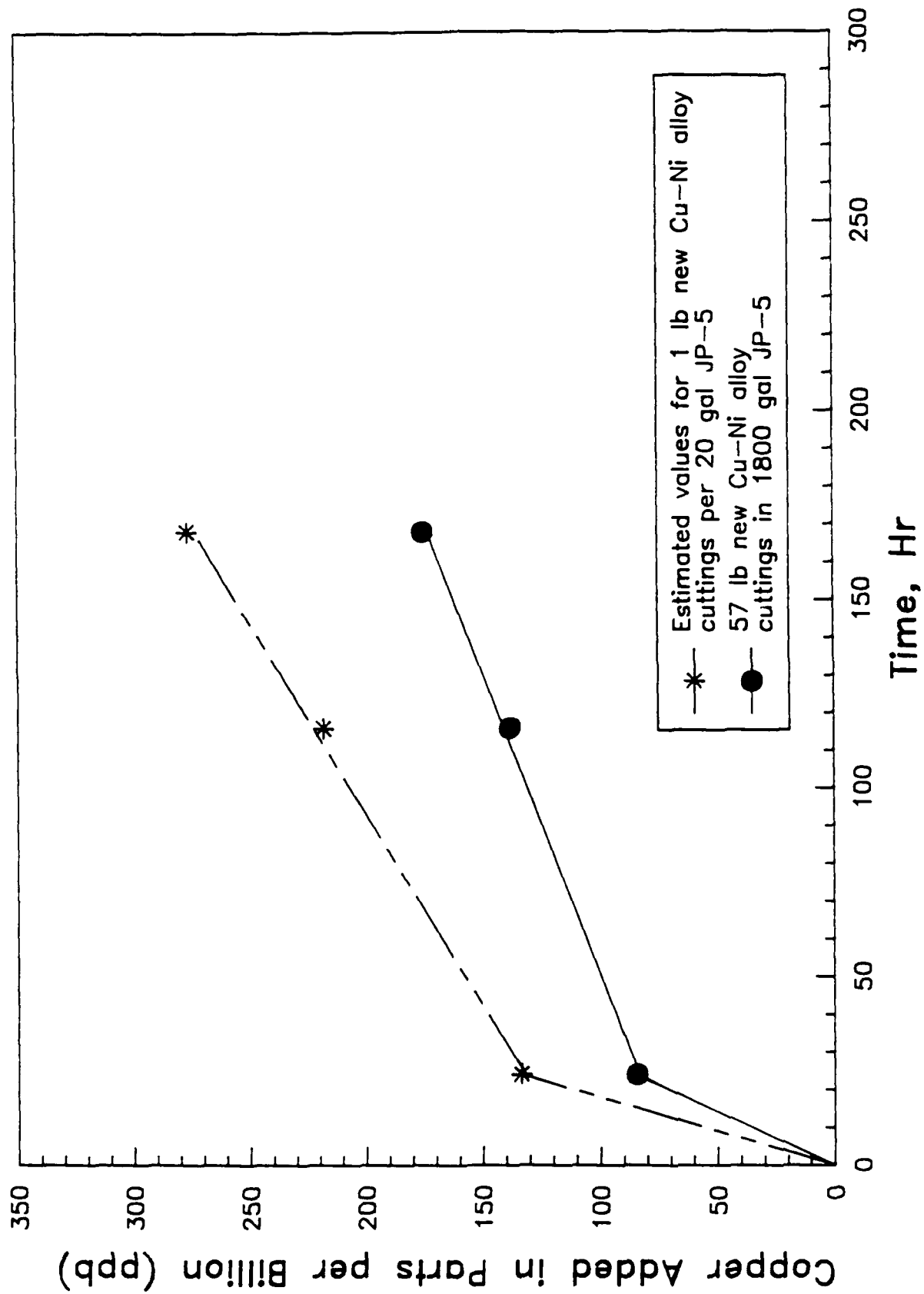


Figure A-1. Copper concentration in fuel as determined by spectrometer

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